

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 United States of America  
 in its capacity as elected Office

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<b>Date of mailing (day/month/year)</b> 18 February 2003 (18.02.03)	
<b>International application No.</b> PCT/JP02/02797	<b>Applicant's or agent's file reference</b> J923-PCT
<b>International filing date (day/month/year)</b> 22 March 2002 (22.03.02)	<b>Priority date (day/month/year)</b> 22 March 2001 (22.03.01)
<b>Applicant</b> KADOWAKI, Yasushi et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

15 October 2002 (15.10.02)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO  
 34, chemin des Colombettes  
 1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.70.10

Authorized officer

Althea NEVERS (Fax 338 7010)

Telephone No. (41-22) 338 8392

10/088488

# PATENT COOPERATION TREATY

## PCT

REC'D 30 JAN 2003

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

(Rationalised Report according to the Notice of the President of the EPO published in the OJ11/2001)

Applicant's or agent's file reference <b>J923-PCT</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/ JP 02/ 02797</b>	International filing date (day/month/year) <b>22/03/2002</b>	Priority date (day/month/year) <b>22/03/2001</b>
International Patent Classification (IPC) or national classification and IPC <b>B01J23/00</b>		<b>RECEIVED</b>
Applicant <b>SHOWA DENKO K. K. et al.</b>		

JUN 02 2003


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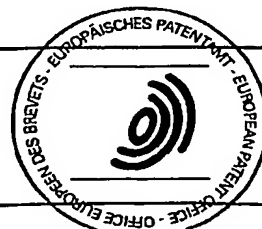
- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This **REPORT** consists of a total of 2 sheets, including this cover sheet.  
☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of \_\_\_\_\_ sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand <b>15/10/2002</b>	Date of completion of this report <b>23/01/2003</b>
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer <b>HOFMANN D G</b> Tel. (+49-89) 2399 2828



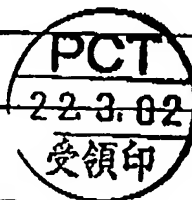
## PCT REQUEST

1/5

Original (for SUBMISSION) - printed on 22.03.2002 04:42:06 PM

J923-PCT

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.92 (updated 01.03.2001)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Japan Patent Office (RO/JP)
0-7	Applicant's or agent's file reference	J923-PCT
I	Title of invention	CATALYST FOR PRODUCING BOTH END-HYDROXYL GROUP-TERMINATED DIOLS, PROCESS FOR PRODUCING THE CATALYST, PROCESS FOR PRODUCING THE DIOLS BY USING THE CATALYST, AND BOTH END-HYDROXYL GROUP-TERMINATED DIOLS OBTAINED BY THE PROCESS
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	SHOWA DENKO K. K.
II-5	Address:	13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 Japan
II-6	State of nationality	JP
II-7	State of residence	JP
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	KADOWAKI, Yasushi
III-1-5	Address:	C/O OITA PLANT, SHOWA DENKO K.K. 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 Japan
III-1-6	State of nationality	JP
III-1-7	State of residence	JP



## PCT REQUEST

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III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	KANEDA, Masato
III-2-5	Address:	C/O OITA PLANT, SHOWA DENKO K.K. 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 Japan
III-2-6	State of nationality	JP
III-2-7	State of residence	JP
III-3	Applicant and/or inventor	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	UCHIDA, Hiroshi
III-3-5	Address:	C/O OITA PLANT, SHOWA DENKO K.K. 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 Japan
III-3-6	State of nationality	JP
III-3-7	State of residence	JP
IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent international Authorities as:	agent
IV-1-1	Name (LAST, First)	ISHIDA, Takashi
IV-1-2	Address:	A. AOKI, ISHIDA & ASSOCIATES Toranomon 37 Mori Bldg., 5-1, Toranomon 3-chome, Minato-ku, Tokyo 105-8423 Japan
IV-1-3	Telephone No.	03-5470-1900
IV-1-4	Facsimile No.	03-5470-1911
IV-2	Additional agent(s)	additional agent(s) with same address as first named agent
IV-2-1	Name(s)	TSURUTA, Junichi; YOSHII, Kazuo; NISHIYAMA, Masaya; HIGUCHI, Sotoji



## PCT REQUEST

J923-PCT

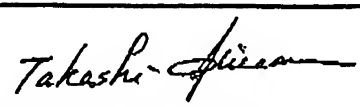
Original (for SUBMISSION) - printed on 22.03.2002 04:42:06 PM

V	Designation / States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT</p> <p>EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT</p> <p>EP: AT BE CH&amp;LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT</p> <p>OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT</p>
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&amp;LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS KE KG KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PH PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW</p>
V-3	National Patent (States which have become party to the PCT after the issuance of this version of EASY)	<p>OM Oman</p> <p>ZM Zambia</p> <p>TN Tunisia</p>
V-5	Precautionary Designation Statement  In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 16 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	22 March 2001 (22.03.2001)
VI-1-2	Number	Patent Application No.2001-081783
VI-1-3	Country	JP

## PCT REQUEST

J923-PCT

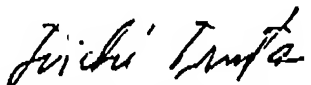
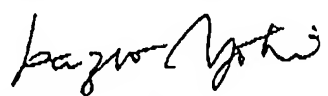
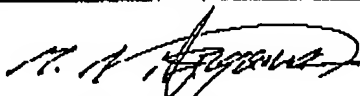

Original (for SUBMISSION) - printed on 22.03.2002 04:42:06 PM

VI-2	Priority claim of earlier national application		
VI-2-1	Filing date	26 March 2001 (26.03.2001)	
VI-2-2	Number	60/278,421	
VI-2-3	Country	US	
VI-3	Priority claim of earlier national application		
VI-3-1	Filing date	07 December 2001 (07.12.2001)	
VI-3-2	Number	Patent Application No. 2001-373977	
VI-3-3	Country	JP	
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	5	-
IX-2	Description	67	-
IX-3	Claims	6	-
IX-4	Abstract	1	EZABST00.TXT
IX-5	Drawings	0	-
IX-7	TOTAL	79	
	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-9	Original separate power of attorney	✓	-
IX-17	PCT-EASY diskette	-	Diskette
IX-18	Other (specified):	translation of power of attorney	-
IX-18	Other (specified):	patent revenue stamps	-
IX-19	Figure of the drawings which should accompany the abstract		
IX-20	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative		
X-1-1	Name (LAST, First)	ISHIDA, Takashi	

## PCT REQUEST

J923-PCT

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X-2	Signature of applicant, agent or common representative	
X-2-1	Name (LAST, First)	TSURUTA, Junichi
X-3	Signature of applicant, agent or common representative	
X-3-1	Name (LAST, First)	YOSHII, Kazuo
X-4	Signature of applicant, agent or common representative	
X-4-1	Name (LAST, First)	NISHIYAMA, Masaya
X-5	Signature of applicant, agent or common representative	
X-5-1	Name (LAST, First)	HIGUCHI, Sotoji

## FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

## FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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## TENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference. <b>J923-PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/JP 02/ 02797</b>	International filing date (day/month/year) <b>22/03/2002</b>	(Earliest) Priority Date (day/month/year) <b>22/03/2001</b>
Applicant <b>SHOWA DENKO K. K.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP 02/02797

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/00 C07C29/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 975 449 A (SUZUKI SHIGETO) 17 August 1976 (1976-08-17) column 1, line 41 -column 4, line 10; example 6 ---	1-14
X	US 2 895 819 A (STUART FIEDLER WILLIAM) 21 July 1959 (1959-07-21) column 1, line 15 - line 41 ---	1-3,6
X	GB 970 790 A (HENKEL & CIE GMBH) 23 September 1964 (1964-09-23) column 2, line 69 -column 3, line 10; table 3 ---	1-5,7
A	US 4 590 313 A (GREY ROGER A ET AL) 20 May 1986 (1986-05-20) the whole document --- -/--	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

18 June 2002

Date of mailing of the international search report

22/07/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Schoofs, B

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP 02/02797

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 581 379 A (DU PONT) 10 December 1980 (1980-12-10) the whole document ----	
A	US 5 744 419 A (CHOUDHARY VASANT RAMCHANDRA ET AL) 28 April 1998 (1998-04-28) the whole document -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 02/02797

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 3975449	A	17-08-1976	NONE		
US 2895819	A	21-07-1959	NONE		
GB 970790	A	23-09-1964	NONE		
US 4590313	A	20-05-1986	NONE		
GB 1581379	A	10-12-1980	BE	862367 A1	27-06-1978
			CA	1105059 A1	14-07-1981
			DE	2758500 A1	29-06-1978
			FR	2376106 A1	28-07-1978
			IT	1089990 B	18-06-1985
			JP	53082712 A	21-07-1978
			NL	7714433 A	30-06-1978
US 5744419	A	28-04-1998	US	6293979 B1	25-09-2001

10 1088485

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 October 2002 (03.10.2002)

PCT

(10) International Publication Number  
**WO 02/076610 A1**

- (51) International Patent Classification?: **B01J 23/00**, C07C 29/00 (74) Agents: **ISHIDA, Takashi** et al.; A. AOKI, ISHIDA & ASSOCIATES, Toranomon 37 Mori Bldg., 5-1, Toranomon 3-chome, Minato-ku, Tokyo 105-8423 (JP).
- (21) International Application Number: PCT/JP02/02797
- (22) International Filing Date: 22 March 2002 (22.03.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
2001-081783 22 March 2001 (22.03.2001) JP  
60/278,421 26 March 2001 (26.03.2001) US  
2001-373977 7 December 2001 (07.12.2001) JP
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): **SHOWA DENKO K. K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **KADOWAKI, Yasushi** [JP/JP]; C/O OITA PLANT, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **KANEDA, Masato** [JP/JP]; C/O OITA PLANT, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **UCHIDA, Hiroshi** [JP/JP]; C/O OITA PLANT, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP).
- Published:**  
— with international search report  
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYST FOR PRODUCING BOTH END-HYDROXYL GROUP-TERMINATED DIOLS, PROCESS FOR PRODUCING THE CATALYST, PROCESS FOR PRODUCING THE DIOLS BY USING THE CATALYST, AND BOTH END-HYDROXYL GROUP-TERMINATED DIOLS OBTAINED BY THE PROCESS

(57) Abstract: A catalyst which contains at least one element selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table, and is to be used for subjecting an epoxy alcohol represented by a general formula (1) to a hydrogenolysis reaction in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds. By use of such a catalyst, a both end-hydroxyl group-terminated diol having a high purity can be produced efficiently.

WO 02/076610 A1



## DESCRIPTION

CATALYST FOR PRODUCING BOTH END-HYDROXYL GROUP-TERMINATED  
DIOLS, PROCESS FOR PRODUCING THE CATALYST, PROCESS FOR  
5 PRODUCING THE DIOLS BY USING THE CATALYST, AND BOTH END-  
HYDROXYL GROUP-TERMINATED DIOLS OBTAINED BY THE PROCESS

This application claims the priority of an  
application based on U.S. Provisional Application Serial  
10 No. 60/278,421 (filed on March 26, 2001).

## Technical Field

The present invention relates to a catalyst for  
producing a diol terminated with a hydroxyl group at both  
15 ends thereof (hereinafter, referred to as "both end-  
hydroxyl group-terminated diol"), a process for producing  
such a catalyst, a process for producing both end-  
hydroxyl group-terminated diols by using the catalyst,  
and both end-hydroxyl group-terminated diols which have  
20 been obtained by such a production process.

More specifically, the present invention relates to  
a catalyst for producing both end-hydroxyl group-  
terminated diols, which is useful when both end-hydroxyl  
group-terminated diols are produced by the hydrogenolysis  
25 of an epoxy alcohol compound; a process for producing the  
catalyst; a process for producing both end-hydroxyl  
group-terminated diols by using the catalyst, and both  
end-hydroxyl group-terminated diols which have been  
obtained by the production process.

30

## Background Art

Both end-hydroxyl group-terminated diols are  
industrially useful as starting materials for resins such  
as polyester resins and polyurethane resins.  
35 Particularly, 1,3-propanediol is a compound having a  
great potential demand as a starting material for  
synthetic resins, particularly as a starting material for

polyester fiber. Therefore, studies are being made to develop a process for producing this compound, at low cost, by a chemical production procedure, a biological production procedure, etc.

5           Heretofore, as the process for chemically producing the 1,3-propanediol, there are known various processes including: a production process for 1,3-propanediol wherein 3-hydroxypropionaldehyde (hereinafter simply referred to as "3-HPA") is synthesized by a hydration  
10           reaction of acrolein and the resultant product is then subjected to a hydrogenation reaction (Unexamined Japanese patent publication ("KOKAI"; hereinafter simply referred to as "JP-A") Hei. 10-212253); and a production process for 1,3-propanediol wherein 3-HPA is synthesized  
15           by a hydroformylation reaction of ethylene oxide and the resultant product is then subjected to a hydrogenation reaction (JP-A Hei. 11-515021); etc.

          In any of these conventional processes, 1,3-propanediol is produced by finally hydrogenating 3-HPA, and therefore, these processes have a problem that  
20           unreacted 3-HPA is liable to remain in the resultant 1,3-propanediol product. In a case where polyester is synthesized by using 1,3-propanediol containing a carbonyl compound such as 3-HPA, it has been pointed out  
25           that such 1,3-propanediol is liable to cause odor or coloring in the polyester.

          Accordingly, the 1,3-propanediol product should preferably contain no carbonyl compound such as 3-HPA, as completely as possible. However, it is difficult to  
30           remove these carbonyl compounds by a general purification method such as distillation, e.g., as disclosed in JP-A Hei. 6-40973 and JP-A Hei. 11-509828, etc.

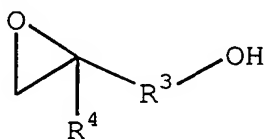
          Under these circumstances, in order to obtain 1,3-propanediol having a low content of carbonyl compounds  
35           such as 3-HPA, JP-A Hei. 6-40973 discloses a method of subjecting 3-HPA to a hydrogenation reaction through two stages, and JP-A Hei. 11-509828 discloses a method of

removing carbonyl compounds which have been contained in 3-HPA by utilizing the reaction of the carbonyl compounds with an alkali. However, in any of these methods, it is difficult to obtain a 100 % conversion for 3-HPA, and therefore it is necessary to remove the carbonyl compounds remaining in the resultant 3-HPA product. Such a removing operation increases the load on the production process for 1,3-propanediol, and this becomes a cause for increasing the production cost of 1,3-propanediol.

For solving the above-mentioned problems, there has been investigated a process for chemically producing 1,3-propanediol while no 3-HPA is used as the starting material. As one of these methods, there is a conceivable method wherein an epoxy alcohol compound (i.e., glycidol in this case) is subjected to hydrogenolysis.

As the reaction for obtaining a diol compound by the hydrogenolysis of an epoxy alcohol, for example, a hydrogenolysis reaction of glycidol by a Pd/C catalyst in methanol has been reported by Sajiki et al., in Journal of Chemical Society, Chemical Communications, pp. 1041-1042 (1999). However, according to this method, only 1,2-propanediol is produced and it is reported that the intended 1,3-propanediol cannot be obtained. In general, it is difficult to obtain such a hydroxyl group-terminated alcohol by the hydrogenolysis of a terminal epoxy group.

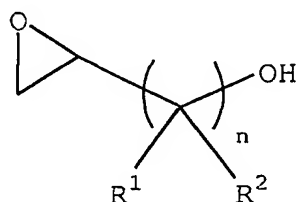
On the other hand, U.S. Patent No. 3,975,449 discloses a process wherein a both end-hydroxyl group-terminated diol is produced by subjecting a hydroxyl group-terminated epoxy alcohol having a di-substituted oxirane ring represented by the following formula (4) to hydrogenolysis in a solvent of water, alcohol or amide.



(wherein R<sup>3</sup> represents an alkylene group having 1 to 5 carbon atoms, and R<sup>4</sup> represents an alkyl group having 1 to 5 carbon atoms or a hydroxyalkyl group having 1 to 5 carbon atoms).

5 However, even in the method disclosed in this Patent publication, the selectivity factor corresponding to the conversion of the hydroxyl group-terminated epoxy alcohols having a mono-substituted oxirane ring represented by general formula (1) into both end-hydroxyl  
10 group-terminated diols is low, and Practical Example 6 of this Patent publication discloses that the selectivity factor corresponding to the conversion from glycidol into 1,3-propanediol is extremely low.

General formula (1):



15

On the other hand, German Patent No. 1,139,477 discloses a process wherein a hydroxyl group-terminated alcohol is produced with a relatively good selectivity by the hydrogenolysis of 1,2-epoxyalkane which is a hydroxyl  
20 group-terminated epoxide having a mono-substituted oxirane ring. This patent publication has achieved an improvement in the selectivity for hydroxyl group-terminated alcohols in the hydrogenolysis of hydroxyl group-terminated 1,2-epoxyalkane having a mono-  
25 substituted oxirane ring, while such an improvement had been difficult until that time.

However, even by this method disclosed in this patent publication, the selectivity is not sufficiently high, unless the substituent of the oxirane ring has 7 or  
30 more carbon atoms, and it is found to be difficult to obtain hydroxyl group-terminated alcohols, similarly to the conventional methods.

As described above, there has never been known a

process wherein an intended both end-hydroxyl group-terminated diol (such as 1,3-propanediol) is efficiently produced by the hydrogenolysis reaction of an epoxy alcohol compound (such as glycidol) with the number of carbon atoms in the substituent thereof being as small as 6 or less, among hydroxyl group-terminated epoxy compounds having a mono-substituted oxirane ring.

#### Disclosure of Invention

An object of the present invention is to provide a novel catalyst for producing both end-hydroxyl group-terminated diols, which is useful in efficiently producing both end-hydroxyl group-terminated diols by the hydrogenolysis reaction of an epoxy alcohol compound.

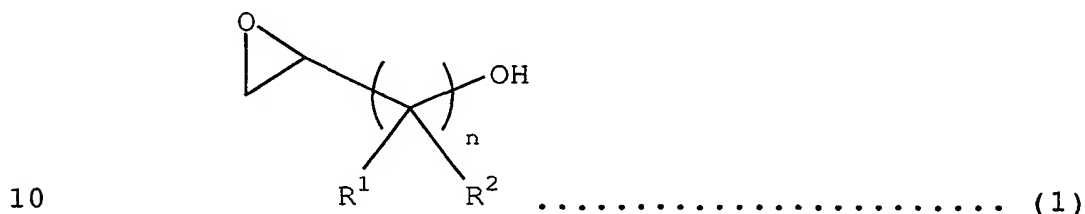
Another object of the present invention is to provide a process for producing the above-mentioned catalyst, a process for producing both end-hydroxyl group-terminated diols by using the catalyst, and both end-hydroxyl group-terminated diols which have been obtained by the above production process.

As a result of earnest study, the present inventors have found that, when a both end-hydroxyl group-terminated diol is intended to be produced by the hydrogenolysis reaction of an epoxy alcohol compound having a mono-substituted oxirane ring with the substituent having 6 or less carbon atoms, the both end-hydroxyl group-terminated diol can be produced with a high selectivity by conducting the hydrogenolysis reaction by use of a catalyst in the presence of a specific solvent. The present invention has been accomplished based on such a discovery.

More specifically, in a first aspect, the present invention relates to a catalyst for producing both end-hydroxyl group-terminated diols, which is usable in a process for producing a both end-hydroxyl group-terminated diol represented by general formula (2) by subjecting an epoxy alcohol compound represented by

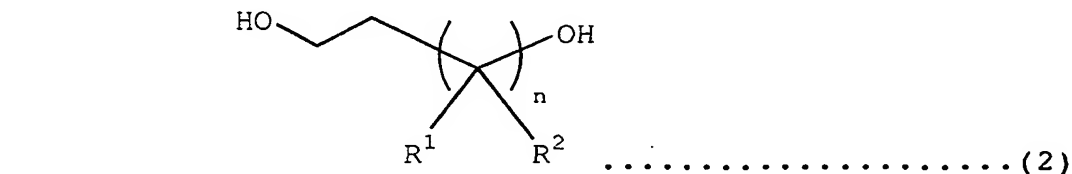
general formula (1) to a hydrogenolysis reaction in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, the catalyst comprising at least one element selected from the group consisting of Group V, Group VI, Group VII, Group VIII, Group IX, Group X and Group XI of the periodic table.

General formula (1):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6);

General formula (2):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6).

In a second aspect, the present invention relates to a process for producing the catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention.

In a third aspect, the present invention relates to a process for producing both end-hydroxyl group-terminated diols by using the catalyst for producing both end-hydroxyl group-terminated diols according to the

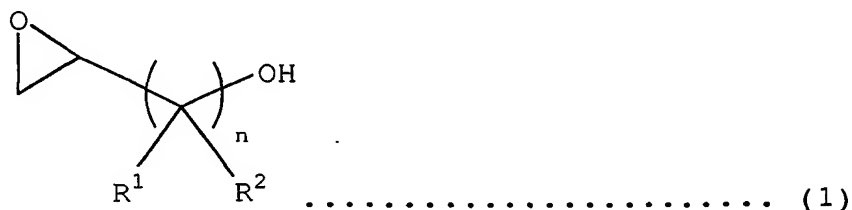
first aspect of the present invention.

Further, in a fourth aspect, the present invention relates to both end-hydroxyl group-terminated diols which have been produced by the process for producing both end-hydroxyl group-terminated diols of the third aspect of the present invention.

In addition, the present invention may include the following embodiments.

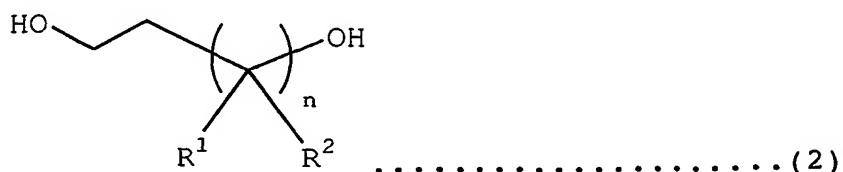
(1) A catalyst which contains at least one element selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table, and is to be used for subjecting an epoxy alcohol represented by the following general formula (1) to a hydrogenolysis reaction in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the following general formula (2).

General formula (1):



(wherein R¹ and R² each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6);

General formula (2):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6).

(2) A catalyst for producing both end-hydroxyl group-terminated diols as described in the above embodiment 1, which comprises at least one element selected from the group consisting of Fe, Co, Ni, Cu, Re and Ru.

(3) A catalyst for producing both end-hydroxyl group-terminated diols as described in the above embodiment (1) or (2), which is a sponge-type catalyst.

(4) A catalyst for producing both end-hydroxyl group-terminated diols as described in the above embodiment (1) or (2), which is a carrier-type catalyst.

(5) A catalyst for producing both end-hydroxyl group-terminated diols as described in the above embodiment 4, wherein the carrier comprises as least one species selected from the group consisting of: activated carbon, alumina, silica, silica alumina, zeolite, diatomaceous earth, titania, and zirconia.

(6) A process for producing a catalyst for producing both end-hydroxyl group-terminated diols as described in the above embodiment (3), which comprises at least the following Step (A) and Step (B):

Step (A): a step of producing an alloy of aluminum and at least one element selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table;

Step (B): a step of eluting aluminum from the alloy obtained in Step (A), to thereby produce a catalyst for producing both end-hydroxyl group-terminated diols.

(7) A process for producing a catalyst for producing both end-hydroxyl group-terminated diols as



described in the above embodiment (4) or (5), which comprises at least the following Step (C) and Step (D):

5        Step (C): a step of causing at least one element or a compound containing the at least one element to be carried on a carrier, the element being selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table, to thereby produce a carrier carrying  
10        thereon the at least one element;

Step (D): a step of hydrogenating the at least one element carried on the carrier obtained in Step (C), to thereby produce a catalyst for producing both end-hydroxyl group-terminated diols.

15        (8) A process for producing a both end-hydroxyl group-terminated diol, wherein an epoxy alcohol represented by the following general formula (1) is subjected to a hydrogenolysis reaction in the presence of a catalyst for producing both end-hydroxyl group-terminated diols according to any of the above  
20        embodiments (1) to (5), in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon  
25        compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the following general formula (2).

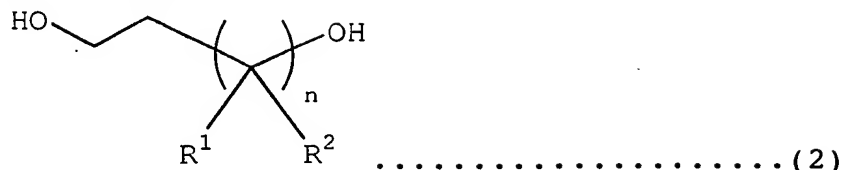
General formula (1):



30        (wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an

integer of 1 to 6);

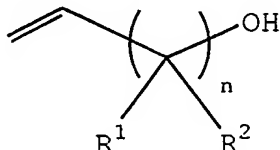
General formula (2):



(wherein  $\text{R}^1$  and  $\text{R}^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6).

(9) A process for producing a both end-hydroxyl group-terminated diol as described in the above embodiment (8), wherein the epoxy alcohol represented by the following general formula (1) is a compound which has been obtained by the epoxidizing an unsaturated alcohol compound represented by formula (3):

General Formula (3):



(wherein  $\text{R}^1$  and  $\text{R}^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6).

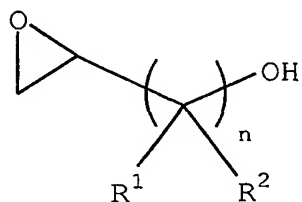
(10) A process for producing a both end-hydroxyl group-terminated diol represented by the general formula (2), which comprises at least the following Step (E) and Step (F):

Step (E): a step of epoxidizing an unsaturated alcohol compound represented by general formula (3), to thereby obtain an epoxy alcohol represented by the general formula (1);

Step (F): a step of subjecting the epoxy alcohol compound to a hydrogenolysis reaction in the presence of

a catalyst for producing a both end-hydroxyl group-terminated diols according to any of claims 1-5, and in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the following general formula (2).

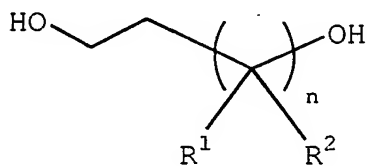
General formula (1):



10 ..... (1)

(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6);

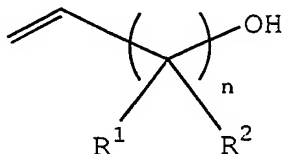
General formula (2):



15 ..... (2)

(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6)

General Formula (3):



25 (wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl

group having 6 to 13 carbon atoms and n represents an integer of 1 to 6);

5 (1). A process for producing a both end-hydroxyl group-terminated diol according to any of the above embodiments (8) to (10), wherein the epoxy alcohol represented by the following general formula (1) is at least one epoxy alcohol compound selected from the group consisting of: glycidol, 3,4-epoxy-1-butanol and 3,4-epoxy-2-butanol.

10 (12) A process for producing a both end-hydroxyl group-terminated diol as described in the above embodiments (9) or (10), wherein the an unsaturated alcohol compound represented by general formula (3) is at least one unsaturated alcohol compound selected from the group consisting of: allyl alcohol, 3-buten-1-ol and 3-buten-2-ol.

20 (13) A process for producing a both end-hydroxyl group-terminated diol according to any of claims 8-12, wherein the solvent is at least one species selected from the group consisting of diethyl ether, dibutyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, 1,4-dioxane, benzene, toluene, xylene, cyclohexane, hexane, ethyl acetate, propyl acetate, isopropyl acetate and butyl acetate.

25 14. A both end-hydroxyl group-terminated diol, which has been produced by a process for producing a both end-hydroxyl group-terminated diol according to any of above embodiments (8) to (13)

### 30 Best Mode for Carrying Out the Invention

Hereinbelow, the present invention will be described in detail with reference to the accompanying drawings as desired. In the following description, "%" and "part(s)" representing a quantitative proportion or ratio are those based on mass, unless otherwise noted specifically.  
35 (Catalyst for producing both end-hydroxyl group-terminated diols)

First, the first aspect of the present invention is described in detail.

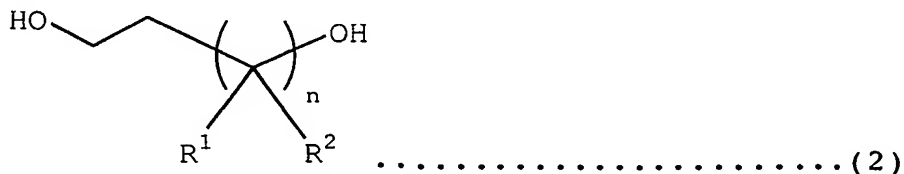
In the first aspect, the present invention relates to a catalyst for producing both end-hydroxyl group-terminated diols, which is usable in a process for producing both end-hydroxyl group-terminated diols represented by general formula (2) by subjecting an epoxy alcohol compound represented by general formula (1) to a hydrogenolysis reaction in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, the catalyst comprising at least one element selected from the group consisting of Group V, Group VI, Group VII, Group VIII, Group IX, Group X and Group XI of the periodic table:

General formula (1):



(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6);

General formula (2):



(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6).

The catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention comprises at least one element selected from the group consisting of Group V, Group VI, Group VII, Group VIII, Group IX, Group X and Group XI of the periodic table. In the present invention, the "periodic table" refers to that according to Nomenclature of Inorganic Chemistry, Revised Edition, 1989, International Union of Pure and Applied Chemistry.

The catalyst may preferably comprise at least one element selected from the group consisting of Cr, Mn, Fe, Co, Ni, Cu, Mo, W, Re and Ru. The catalyst may more preferably comprise at least one element selected from the group consisting of Fe, Co, Ni, Cu, Re and Ru.

According to the present inventors' investigation, it is presumed that the reason why such elements are effective as a catalyst for producing both end-hydroxyl group-terminated diols is that such an element has a high affinity for the oxygen atom of the epoxy group of a reactant (or substrate) compound, and therefore this affinity facilitates the cleavage wherein the bonding between the oxygen atom and secondary or tertiary carbon is cleaved via a radical or a carbonium ion.

The catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention may contain any element other than the above-described elements or any compound, as long as it does not substantially inhibit the intended reaction. In view of the catalyst activity, the above-mentioned at least one element selected from the group consisting of Group V, Group VI, Group VII, Group VIII, Group IX, Group X and Group XI of the periodic table may preferably be contained in the catalyst in an amount of 1 % or more, more preferably 2 % or more, particularly preferably 5 % or more (based on the total mass of the catalyst including the at least one element per se).

The form or shape of the catalyst for producing both

end-hydroxyl group-terminated diols according to the first aspect of the present invention is not particularly limited and may be either of the homogeneous-type catalyst or heterogeneous-type catalyst. In view of the ease in the operation of separating the catalyst from the reaction mixture after the reaction, the heterogeneous catalyst is preferred. However, the homogeneous catalyst is also usable in the present invention.

(Homogeneous catalyst)

The homogeneous catalyst may have any form or shape, as long as the catalyst can be dissolved in a reaction mixture at the time of the reaction. More specifically, for example, the catalyst may have a salt form of the element, such as chloride, bromide, iodide, nitrate, sulfate, carboxylate or carbonate, or a so-called complex form where a ligand is bonded to the element.

(Ligand)

In the present invention, the ligand which is usable in the formation of a complex is not particularly limited, and the ligand may be at least one species selected from known ligands. Specific examples thereof may include: carbonyl ligands; phosphorus-containing ligands such as triphenylphosphine, trimethylphosphine, triphenyl phosphite and triphenylphosphine oxide; nitrogen-containing ligands such as ammonia, ethylenediamine and pyridine; ether ligands such as diethyl ether, ethylene glycol dimethyl ether, tetrahydrofuran and 1,4-dioxane; olefin ligands such as ethylene, 1,4-cyclooctadiene and cyclopentadienyl anion; diketonate ligands such as acetylacetonate anion; cyano ligands; halogen ligands such as chloro, bromo and iodo; alkoxide ligands such as methoxide, ethoxide, butoxide and phenoxide; hydride ligands; and ligands comprising a combination of at least two species of the above-mentioned ligands. Of course, the ligands usable in the present invention are not limited to these specific ligands.

(Use of homogeneous catalyst)

The homogeneous catalyst may be used in an embodiment wherein the catalyst is preliminarily dissolved in a solvent and then the resultant mixture is used for the reaction, or the catalyst may be used in an embodiment wherein it is preliminarily dissolved in the reactant epoxy alcohol and then the resultant mixture is used for the reaction. Alternatively, it is also possible that the catalyst is simultaneously charged to a reaction system together with a solvent and starting material, and then the resultant mixture is subjected to the reaction. Further, it is also possible that the catalyst dissolved in a solvent is preliminarily brought into contact with hydrogen so as to be activated, and then the activated catalyst is subjected to the reaction with an epoxy alcohol.

(Heterogeneous catalyst)

In the case of the heterogeneous catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention, the form or shape of the element or compound usable in the catalyst is not particularly limited. The heterogeneous catalyst may preferably be used in any form of a metal type, a sponge type, an oxide, a hydroxide, a boride, a phosphide, etc.

With respect to the element to be contained in the catalyst according to the first aspect of the present invention, an element in the above-described form or a compound containing the element may be used as it is in the intended reaction, or such an element or compound may be used in the reaction as a so-called carrier-type catalyst which has been obtained by causing the element or compound to be carried on an appropriate carrier (or support).

(Sponge-type catalyst)

In a case where the element is used as it is as the catalyst for producing both end-hydroxyl group-terminated



diols according to the first aspect of the present invention, one preferred example of the catalyst is a sponge-type catalyst. The term "sponge-type catalyst" as used herein means a porous metal-containing catalyst.

5 "Sponge Ni" which is one example of the sponge-type catalyst is described, for example, in Tetrahedron Lett., Vol. 32, No. 40, pp. 5885-5888 (1999).

Further, as the element or compound containing the element, which is usable as it is as the catalyst,  
10 examples thereof may include: sponge catalysts such as sponge Fe, sponge-Co, sponge-Ni, sponge-Cu and sponge-Ru; oxide catalysts such as V oxide, Cr oxide, Fe oxide, Co oxide, Ni oxide, Cu oxide, Mo oxide, W oxide, Re oxide, Ru oxide, Rh oxide, Pd oxide, Pt oxide, Cr oxide-Fe  
15 oxide, Cr oxide-Cu oxide, Cr oxide-Ni oxide, Cr oxide-Zn oxide and Cr oxide-Cu oxide-Zn oxide; hydroxide catalysts such as Cr hydroxide, Mn hydroxide, Fe hydroxide, Co hydroxide, Ni hydroxide, Cu hydroxide, Ru hydroxide, Rh hydroxide, Pd hydroxide and Pt hydroxide; boride  
20 catalysts such as Co boride and Ni boride; and phosphide catalysts such as Ni phosphide. These catalysts may be used individually or in combination of two or more species thereof.

(Carrier-type catalyst)

25 In a case where the catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention is a carrier-type catalyst, the carrier usable in such an embodiment is not particularly limited and may appropriately be selected  
30 from known carriers. Specific examples thereof may include: activated carbon (hereinafter sometimes simply referred to as "carbon"), silica, alumina, silica alumina, zeolite, titania, zirconia, magnesia, diatomaceous earth (or kieselguhr), barium sulfate,  
35 barium carbonate, calcium carbonate and magnesium carbonate. Among these, it is preferred to use activated carbon, silica, alumina, silica alumina, zeolite,

titania, zirconia and diatomaceous earth, in view of the effect thereof on reaction, the surface area at the preparation of the catalyst or the industrial practicability such as strength of carrier.

5           In a case where an element or a compound containing the element, which is the active species of the catalyst, is caused to be carried on a carrier, the amount of the element or compound containing the element and the carrier are preferably such that the amount of the  
10           element or compound containing the element is from 0.01 to 150 mass % (or % by mass) based on the total mass of the carrier. If the amount of the element or compound containing the element is less than 0.01 mass %, the concentration of active sites of the catalyst is  
15           relatively low and, therefore, a sufficiently high catalytic activity which is practically acceptable cannot be obtained and such an amount is not preferred. On the other hand, if the amount exceeds 150 mass %, the effect of the carrier cannot be exhibited sufficiently, and such  
20           an amount is not preferred.

          The amount of the element or compound containing the element is more preferably from 0.05 to 100 mass %, more preferably from 0.1 to 90 mass %, particularly from 0.3 to 30 mass %.

25           Specific examples of the carrier-type catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention may include: Cr oxide-alumina, Cr oxide-silica, Cr oxide-silica alumina, Cu oxide-alumina, Cu oxide-silica, Mo  
30           oxide-alumina, Mo oxide-silica, Re-alumina, Re-silica, Re-activated carbon, Co-diatomaceous earth, Co-alumina, Co-silica, Co-silica alumina, Co-carbon, Ni-diatomaceous earth, Ni-alumina, Ni-silica, Ni-silica alumina, Ni-carbon, Ni-Cu-alumina, Ru-alumina, Ru-silica, Ru-silica  
35           alumina, Ru-carbon, Pd-alumina, Pd-silica, Pd-silica alumina, Pd-carbon, Pd-barium sulfate, Pd-calcium carbonate, Pt-alumina, Pt-silica, Pt-silica alumina, Pt-

carbon, etc. These catalyst may be used individually or in combination of two or more species thereof.

Among the catalysts for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention, the heterogeneous catalyst may most preferably be a sponge-type or carrier-type catalyst containing at least one element selected from the group consisting of Fe, Co, Ni, Cu, Re and Ru, and/or a compound containing at least one of these elements.

The shape, form, size, etc., of these catalysts are not particularly limited. Specific examples of the shape or form of the catalyst may include: powder-type, solid ground or crushed product-type, flake-type, spherical molded article-type, columnar molded article-type and circular molded article-type. With respect to the size of the catalyst, it is possible to use a catalyst having an average particle size of 1 to 1,000  $\mu\text{m}$ , preferably about 10 to 200  $\mu\text{m}$ , in the case of the suspension or fluidized bed-type reaction. In the case of the fixed bed-type reaction, it is possible to use a catalyst having an average particle size of about 1 to 20 mm, preferably 3 to 15 mm.

In the case of the suspension or fluidized bed-type reaction, if the average particle size of catalyst is less than the above-described range (i.e., 1 to 1,000  $\mu\text{m}$ ), there can be caused difficulty in separating the catalyst after the reaction. On the other hand, if the particle size exceeds this range (i.e., 1 to 1,000  $\mu\text{m}$ ), it is possible that the reaction is not conducted efficiently due to the precipitation of the catalyst. In the case of a fixed bed-type reaction, if the average particle size is less than the above-described range (i.e., about 1 to 20 mm), clogging or plugging of the catalyst layer or an increase in the differential pressure is liable to occur. On the other hand, if the particle size exceeds this range (i.e., about 1 to 20

mm), the surface area of the catalyst per the unit volume of a reactor is liable to decrease and this can disadvantageously cause a reduction in the reaction efficiency.

5           Among the catalysts for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention, the shape or form and the particle size of the heterogeneous catalyst may appropriately be selected in view of the suitability for the reaction  
10           type.

(Production process for catalyst)

          The second aspect of the present invention is described below. The second aspect of the present invention relates to a process for producing the catalyst  
15           for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention.

          The process for producing the catalyst for producing both end-hydroxyl group-terminated diols according to the second aspect of the present invention may be conducted  
20           by selecting an optimal method in view of the catalyst for producing both end-hydroxyl group-terminated diols, which is to be produced in this process. In the preparation of this catalyst, it is possible to use any of those processes which, per se, are known in the art.

25           In a case where the catalyst for producing both end-hydroxyl group-terminated diols is a sponge-type catalyst or a carrier-type catalyst, each of these catalysts can be produced by a production process comprising the following steps. Of course, in the present invention,  
30           the production process for the catalyst is not limited to these specific processes, but the catalysts may be produced by any of those processes which, per se, are known in the art.

          For example, the sponge-type catalyst can be  
35           produced by a production process comprising the following Step (A) and Step (B):

Step (A): a step of producing an alloy of aluminum

and at least one element selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table;

Step (B): a step of eluting aluminum from the alloy obtained in Step (A), to thereby produce a catalyst for producing both end-hydroxyl group-terminated diols.

The carrier-type catalyst can be produced by a production process comprising the following Step (C) and Step (D):

Step (C): a step of causing at least one element or a compound containing the at least one element to be carried on a carrier, the element being selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table, to thereby produce a carrier carrying thereon the at least one element;

Step (D): a step of hydrogenating the at least one element carried on the carrier obtained in Step (C), to thereby produce a catalyst for producing both end-hydroxyl group-terminated diols.

Further, with respect to the catalysts other than the sponge-type catalyst and the carrier-type catalyst, for example, a metal-type catalyst can be produced by a process wherein a salt, an oxide, a hydroxide, etc., of a metal is treated with a reducing agent such as hydrogen. An oxide or hydroxide catalyst can be produced by a process wherein a metal hydroxide or oxide is precipitated by using an alkali, etc., in a metal salt solution, or a method wherein the resultant precipitate is calcined. A boride catalyst can be produced by a process wherein a metal salt is treated with tetrahydroborate. Further, a phosphide catalyst can be produced by a process wherein a metal solution is treated with a phosphite.

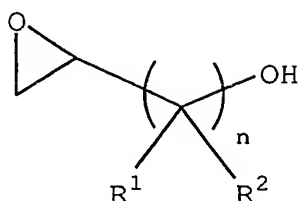
In the case of carrier-type catalyst, examples of the production process may include: in addition to the above-describe production processes, a method wherein a hydroxide or oxide of a metal is deposited on a carrier, and the resultant carrier is calcined; a method wherein a carrier is impregnated with a metal salt solution, and the resultant carrier is calcined; a method wherein a carrier having thereon a deposited metal hydroxide or oxide, or a carrier impregnated with a metal salt solution is calcined and then is reduced with a reducing agent, to thereby prepare a catalyst.

In any case, the second aspect of the present invention is not limited to the above-mentioned specific processes, but any process may be used as long as it can produce the catalyst for producing both end-hydroxyl group-terminated diols according to the first aspect of the present invention.

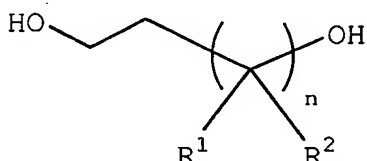
(Production process for both end-hydroxyl group-terminated diol)

The third aspect of the present invention is described below. The third aspect of the present invention relates to a process for producing both end-hydroxyl group-terminated diols, wherein an epoxy alcohol represented by the following general formula (1) is subjected to a hydrogenolysis reaction in the presence of a catalyst for producing both end-hydroxyl group-terminated diols according to any of claims 1-5, in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the following general formula (2).

General formula (1):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6);



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6).  
(Epoxy alcohol)

The compound represented by the general formula (1) to be used in the process for producing both end-hydroxyl group-terminated diols according to the third aspect of the present invention is an epoxy alcohol compound. More specifically, the compound represented by the general formula (1) may include: a compound where a mono-substituted oxirane ring and a hydroxyl group are bonded through a methylene chain having 1 to 6 carbon atoms, or a methylene chain having 1 to 6 carbon atoms which has been substituted with a cycloalkyl group, an aryl group or an alkyl group having 1 to 8 carbon atoms.

Specific examples of the epoxy alcohol compound may include: glycidol, 3,4-epoxy-2-butanol, 1,2-epoxy-3-pentanol, 1,2-epoxy-3-hexanol, 1,2-epoxy-3-heptanol, 2-methyl-3,4-epoxy-2-butanol, 1-phenyl-2,3-epoxy-1-propanol, 1-cyclohexyl-2,3-epoxy-1-propanol, 3,4-epoxy-1-butanol, 4,5-epoxy-1-pentanol, 5,6-epoxy-1-hexanol and

7,8-epoxy-1-octanol. However, the epoxy alcohol compounds usable in the present invention are not limited to these specific compounds.

Among these, glycidol, 3,4-epoxy-1-butanol and 3,4-epoxy-2-butanol are preferred in view of easy availability thereof, the industrial value of the both end-hydroxyl group-terminated diol as the reaction product, etc.  
(Solvent)

The process for producing both end-hydroxyl group-terminated diols according to the third aspect of the present invention has a purpose of producing the both end-hydroxyl group-terminated diols with a high selectivity by the regioselective (or regiospecific) hydrogenolysis reaction of the epoxy ring of an epoxy alcohol and is characterized in that the reaction is conducted by using a solvent having a low polarity.

As described above, conventionally reported hydrogenolysis reactions of an epoxy alcohol have been conducted in a solvent having a hydroxyl group, such as water or alcohol. However, the use of such a polar solvent causes, as a side reaction, a ring-opening reaction of the epoxy ring due to the solvent molecule. Therefore, the known reaction can disadvantageously decrease the hydrogenolysis selectivity corresponding to the conversion of the epoxy alcohol into a hydroxyl group-terminated alcohol which is intended to be obtained.

As a result of the present inventors' study, it has been found that when a low-polarity solvent having no hydroxyl group is used, not only the ring-opening reaction of the epoxy ring due to the solvent molecule, which is a side reaction, is not substantially produced, but also the regioselectivity of the hydroxyl group provided by the ring opening of the epoxy ring is elevated, that is, the ratio of the hydroxyl group-terminated alcohol to be produced is increased, so that



such a process is advantageous as the process for producing the both end-hydroxyl group-terminated diols. According to the present inventors' investigation, it is presumed that the reason why the selectivity is increased by the use of a low-polarity solvent is that, when a low-polarity solvent is used, the interaction between the solvent molecule and the hydroxyl group of the epoxy alcohol is decreased and reversely the hydroxyl group is oriented toward the catalyst surface side. The steric relationship provided by such an orientation seems to function advantageously for producing the both end-hydroxyl group-terminated diols, in view of the interaction between the catalyst active site and the oxygen atom of the epoxy ring. At the present stage, however, the details of such a phenomenon are not necessarily clear.

Further, in the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention, the use of a solvent is preferred also in view of the control of the ring-opening reaction of the epoxy ring due to dilution therewith, the removal of the heat of reaction, or prevention of a decrease in the hydrogen diffusion efficiency which can be caused due to an increase in the viscosity of the reaction system.

(Examples of solvent)

Specific examples of the solvent usable in the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention may include: ether solvents such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, tetrahydrofuran and 1,4-dioxane;

aromatic hydrocarbon solvents such as benzene,

toluene and xylene;

alicyclic hydrocarbon solvents such as cyclohexane and methylcyclohexane;

5 aliphatic hydrocarbon solvents such as pentane, hexane, heptane and octane;

ester solvents such as methyl formate, ethyl formate, butyl formate, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate and butyl acetate; and

10 halogenated hydrocarbon solvents such as dichloromethane, chloroform and 1,2-dichloroethane.

These solvents may be used individually or as a mixed solvent of two or more species thereof.

Among these, in view of the selectivity for the both end-hydroxyl group-terminated diols in the hydrogenolysis  
15 reaction in the process according to the third aspect of the present invention and the simple and easy availability and easy handleability, it is preferred to use diethyl ether, dibutyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, 1,4-  
20 dioxane, benzene, toluene, xylene, cyclohexane, hexane, ethyl acetate, propyl acetate, isopropyl acetate and butyl acetate. It is more preferred to use diethyl ether, ethylene glycol dimethyl ether, 1,4-dioxane, toluene, cyclohexane, hexane and ethyl acetate.

25 In the third aspect of the present invention, the amount of the solvent to be used is not particularly limited. In general, the solvent may be used in such a range that the concentration of the epoxy alcohol as a reactant becomes 1 to 100 mass %, based on the mass of  
30 the epoxy alcohol as a reactant toward the sum the epoxy alcohol as a reactant and the solvent. If the epoxy alcohol concentration is less than 1 mass %, a practically acceptable reaction rate is less liable to be obtained, or the load for the separation and purification  
35 of the product from the reaction mixture containing the solvent becomes heavier, and therefore such an amount of the solvent may be disadvantageous. On the other hand,

if the epoxy alcohol concentration exceeds 100 mass %, it is possible that the effect of the solvent is not fully exhibited and therefore such an amount may be disadvantageous. The epoxy alcohol concentration may preferably be 3 to 100 mass %, more preferably from 5 to 100 mass %.

(Hydrogenolysis reaction)

In the third aspect of the present invention, the hydrogenolysis reaction of the epoxy alcohol can be conducted by contacting the epoxy alcohol with hydrogen in the presence of a catalyst. As the reaction type, it is possible to use any of known reaction types to be used for hydrogenolysis reaction or hydrogenation reaction, such as continuous-type reaction or batch-type reaction. The catalyst to be used in this embodiment may be either a homogenous catalyst or a heterogeneous catalyst. The form of the catalyst is not particularly limited and an appropriate form may be selected depending on the type of the reaction.

Specific examples of the reaction type to be used in the third aspect of the present invention may include: in the case of a homogeneous catalyst, a simple stirring tank, a bubble tower-type reaction tank and a tubular reaction tank. Specific examples of the reaction type may include: in the case of a heterogeneous catalyst, a suspension-bed simple stirring tank, a fluidized-bed bubble tower-type reaction tank, a fluidized-bed tubular reaction tank, a fixed-bed liquid phase flow-system tubular reaction tank, and a fixed-bed trickle bed-system tubular reaction tank. However, the reaction types usable in the present invention are not limited to these specific reaction types.

In the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention, the amount of the catalyst to be used for the hydrogenolysis reaction varies depending on the reaction type and is not particularly limited. For

example, in the case of batch reaction, the amount of the homogeneous catalyst used may usually be 0.001 to 10 mass %, preferably 0.01 to 5 mass %, more preferably 0.01 to 3 mass %, based on the reactant epoxy alcohol solution.

5 The amount of the heterogeneous catalyst to be used may usually be 0.01 to 100 mass %, preferably 0.1 to 70 mass %, more preferably 0.1 to 50 mass %, based on the reactant epoxy alcohol compound.

10 If the amount of the catalyst is small, a practically sufficient reaction rate may not be obtained. On the other hand, if the amount of the catalyst is large, a reduction in the reaction yield or an increase in the catalyst cost may undesirably be provided due to an increase in the occurrence of the side reaction.

15 In the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention, the hydrogen pressure at the hydrogenolysis reaction is not particularly limited. The reaction may be conducted either under atmospheric pressure condition or under a pressurized condition. In order to efficiently promote the reaction, the reaction may preferably be conducted under a pressurized condition. The pressure, in terms of the gauge pressure, may usually be in the range of 0 to 50 MPa, preferably 0 to 40 MPa, more preferably 0 to 30 MPa.

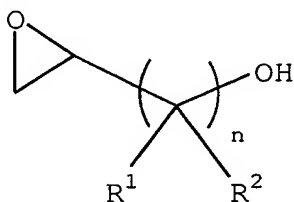
20 In the third aspect of the present invention, the hydrogenolysis reaction may be conducted at any temperature within a range such that it does not substantially decrease the reaction efficiency due to the catalyst. The reaction may usually be conducted at 0 to 200°C, preferably 0 to 180°C and more preferably 0 to 150°C. If the reaction temperature is less than 0°C, the hydrogenolysis reaction may not proceed at a practically acceptable reaction rate. On the other hand, if the temperature exceeds 200°C, the ring opening reaction of the epoxy ring in the epoxy alcohol compound represented by the general formula (1) is more liable to proceed due

the reaction of the starting material epoxy alcohol compounds represented by the general formula (1) with each other, or the reaction between the product both end-hydroxyl group-terminated diol compound represented by the general formula (2) and the epoxy alcohol compound, so that undesired by-products may be disadvantageously produced.

(Epoxy alcohol)

The epoxy alcohol compound represented by the general formula (1) to be used in the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention may be one which has been prepared by any method.

General formula (1):



(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6).

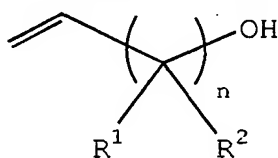
Specific examples of the reaction for obtaining the epoxy alcohol compound represented by the general formula (1) may include: a preparation process wherein an unsaturated alcohol is epoxidized (examined Japanese Patent publication (JP-B) Sho. 51-18407); a process wherein an epoxy alcohol is prepared through the hydrolysis of an epichlorohydrin to produce monochlorohydrin and subsequently the resultant monochlorohydrin is subjected to a ring-closing reaction (Journal of American Chemical Society, Vol. 52, page 1521 (1930)); a preparation process wherein the carbon-carbon double bond of acrolein is epoxidized and the aldehyde group thereof is hydrogenated (U.S. Patent No.

3,041,356); and a preparation process using transesterification between glycidyl esters and alcohols (JP-A Hei. 50-126609). Of course, the reaction for obtaining the epoxy alcohol compound usable in the present invention is not limited to these specific processes.

Among these production processes, the epoxy alcohol compound represented by the general formula (1) to be used in the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention may preferably be an epoxy alcohol compound which has been obtained by the epoxidation reaction of an unsaturated alcohol, in view of the industrial importance or in view of a lower possibility of contamination due to industrially undesired impurities (such as chlorine-containing compound and aldehyde compound) which can function as a poisoning substance to the catalyst for the hydrogenation reaction.

The epoxy alcohol compound represented by the general formula (1) to be used in the third aspect of the present invention may preferably be an epoxy alcohol compound represented by the general formula (1) which has been obtained by the epoxidation reaction of an unsaturated alcohol compound represented by formula (3):

General Formula (3):



(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6).

Specific examples of the unsaturated alcohol represented by formula (3) may include: allyl alcohol, 3-buten-1-ol and 3-buten-2-ol. However, the unsaturated

alcohols usable in the present invention are not limited to these specific compounds.

5 In a case where the epoxy alcohol compound represented by the general formula (1) which has been obtained by the epoxidation reaction of an unsaturated alcohol compound represented by formula (3) is used in the process for producing the both end-hydroxyl group-terminated diols according to the third aspect of the present invention, it is naturally possible that after 10 the epoxidation reaction of an unsaturated alcohol compound, the produced epoxy alcohol is subjected to separation and purification by an operation such as distillation, and the thus obtained purified epoxy alcohol is used as the starting material for the 15 hydrogenolysis reaction. In addition, it is also possible that the reaction mixture containing the epoxy alcohol compound which has been obtained by the epoxidation reaction of the unsaturated alcohol compound is used as the starting material as it is (i.e., 20 substantially without purification), and the resultant reaction mixture is subjected to hydrogenolysis reaction so as to provide the both end-hydroxyl group-terminated diol.

25 In the above-described third aspect of the present invention, e.g., when 1,3-propanediol is produced from glycidol, the product glycidol may be obtained at a conversion (rate) for the glycidol of 60 % or more under a desirable condition, and 70 % to 100 % under a more desirable condition. In this case, the selectivity 30 factor for the 1,3-propanediol may be 60 % or more under a desirable condition.

Herein, the conversion X and selectivity factors S are defined in the following manner.

35 Conversion X = (Moles of reacted reactant in raw material)/(moles of reactant in raw material)

Selectivity factor S = (Moles of reactant which has

been obtained by calculating  
moles of intended product in  
terms of reactant)/(moles of  
reacted reactant)

5 (Both end-hydroxyl group-terminated diol)

The fourth aspect of the present invention is  
described below. The fourth aspect of the present  
invention relates to a both end-hydroxyl group-terminated  
diol which has been produced by the process for producing  
10 the both end-hydroxyl group-terminated diols according to  
the third aspect of the present invention.

In the process for producing the both end-hydroxyl  
group-terminated diols according to the third aspect of  
the present invention, the diol has been obtained by the  
15 hydrogenolysis reaction of an epoxy alcohol, and  
therefore, the product both end-hydroxyl group-terminated  
diol contains substantially no carbonyl compound as an  
impurity. Accordingly, the both end-hydroxyl group-  
terminated diol according to the fourth aspect of the  
20 present invention can provide an effect such that when  
polyester, etc., is produced by using such a diol, the  
generation of coloring or malodor attributable to the  
carbonyl compound can be suppressed to a low level.

For example, whether a carbonyl compound is  
25 contained in the both end-hydroxyl group-terminated diol  
can be confirmed by the following methods:

1) the quantitative determination of known  
carbonyl compounds using gas chromatography, liquid  
chromatography or gas chromatography/mass spectrometry;

30 2) the confirmation of stretching vibration peak  
of C=O in the vicinity of 1,600 to 1,800  $\text{cm}^{-1}$  using IR  
spectrum; or

3) the quantitative determination (ASTM E411-70)  
of a solution containing a condensation product from the  
carbonyl compound and 2,4-dinitrophenylhydrazine, using  
35 the visible-ray spectrum.

In the present invention, the amount of the carbonyl



compound in the obtained product may preferably be less than 500 ppm, more preferably less than 100 ppm. The amount of the carbonyl compound may be measured, e.g., by qualitative determination according to ASTM E411-70 wherein a solution of the condensation product between the carbonyl compound and 2,4-dinitrophenyl hydrazine is qualitatively analysed by using the visible spectrum, etc.

#### Examples

Hereinbelow, the present invention will be described in more detail with reference to Examples and Comparative Examples. Of course, the present invention are not limited to these specific Examples.

In the following Examples, each of reactions was analyzed by using gas chromatography (hereinafter simply referred to as "GC") under the following conditions.

#### GC Analysis Conditions

Apparatus: GC-17A (mfd. by Shimadzu Corporation)

Column: FFAP, inside diameter 0.25 mm $\phi$   $\times$  length 30 m (mfd. by J&W Co.)

Carrier gas : He 1 ml/min, split ratio: 1/30

Detector: FID (Hydrogen flame ionization detector)

Column temperature: (temperature increasing conditions) Retention at 40°C for ten minutes, thereafter temperature increase at a rate of 10°C/minute to 200°C, and then retention at 200°C for 25 minutes

Injection temperature: 230°C

Amount of injected sample: 0.2  $\mu$ l

#### Example 1

2.0 g of sponge-Ni catalyst (trade name: R-200, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of methanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from

the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of methanol to effect the solvent replacement. The  
5 resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of dioxane and 5.00 g of glycidol were added thereto.

The reactor (vessel) was tightly closed and an  
10 operation of pressurizing the inside of the autoclave to 1.0 MPa (gauge pressure) with nitrogen and then depressurizing the inside of the autoclave to 0.0 MPa (gauge pressure) was repeated 5 times to replace the air in the autoclave with nitrogen. Further, the nitrogen  
15 was replaced with hydrogen by the same operation, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the  
20 reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the  
25 contents of the autoclave were replaced with nitrogen, and the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area  
30 ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 76.6 %, the selectivity for 1,3-propanediol was 57.6 % and the selectivity for 1,2-propanediol was 41.3 %. Further, according to the GC analysis, peaks corresponding to 3-  
35 hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 2

2.0 g of sponge-Ni catalyst (trade name: R-200, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an  
5 internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted  
10 three times except for using 20 ml of cyclohexane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of cyclohexane and 5.00 g of glycidol were added  
15 thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of  
20 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction,  
25 hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen,  
30 and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 100 %, the selectivity for 1,3-propanediol was 30.8 % and the  
35 selectivity for 1,2-propanediol was 41.3 %. Further,

according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 3

5           2.0 g of sponge-Ni catalyst (trade name: R-200, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an  
10           internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted  
15           three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

20           The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the  
25           autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to  
30           maintain the reaction pressure at a constant level.

          When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the  
35           supernatant was removed from the autoclave and the supernatant was analyzed by GC.

          As a result of the calculation from the peak area

ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 91.7 %, the selectivity for 1,3-propanediol was 40.4 % and the selectivity for 1,2-propanediol was 46.6 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Comparative Example 1

2.0 g of sponge-Ni catalyst (trade name: R-200, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, and then the resultant supernatant was removed from the autoclave by decantation. Thereafter, 20 g of water and 5.24 g of glycidol were added to the wetted catalyst.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 60°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 88.6 %, the selectivity for 1,3-propanediol was 9.9 % and the

selectivity for 1,2-propanediol was 71.9 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

5 As described above, based on the comparison between the results obtained in Examples 1 to 3 and Comparative Example 1, it may be understood that when the hydrogenolysis reaction of glycidol is conducted in a water solvent, the selectivity for 1,3-propanediol was  
10 extremely low. On the contrary, when a solvent having a lower polarity is used, the selectivity for 1,3-propanediol can remarkably be increased.

Example 4: preparation of sponge-Co catalyst

In a 50 ml-volume glass beaker, 1.3 g of sodium  
15 hydroxide was dissolved in 10.9 g of water and, to the resultant solution, 1.0 g of sponge-Co (Co content: 50 mass %, mfd. by Wako Pure Chemical Industries, Ltd.) was gradually added over 10 minutes while the mixture was being stirred with a magnetic stirrer. After the  
20 addition of the sponge-Co, the glass beaker was immersed in a hot water bath and the reaction was conducted at 50°C for another 1 hour.

The resultant supernatant was removed from the glass beaker by decantation, 20 ml of water was added to the  
25 resultant catalyst. The resultant mixture was stirred, and thereafter, the supernatant was removed from the glass beaker. This water washing operation was repeated until the pH of the supernatant reached 7 to thereby prepare a sponge-Co catalyst suspended in water.

30 Example 5

The sponge-Co catalyst wetted with water, which had been prepared in Example 4 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal  
35 volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave

by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,4-dioxane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,4-dioxane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 95.4 %, the selectivity for 1,3-propanediol was 50.6 % and the selectivity for 1,2-propanediol was 6.0 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 6

30.2 g of dimethoxyethane was placed in an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 5.0 g of glycidol was added thereto, and

thereafter, 0.50 g of 5 % Ru-carbon catalyst (mfd. by NE Chemcat K.K.) was gradually added to the autoclave.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 100°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 50.7 %, the selectivity for 1,3-propanediol was 19.5 % and the selectivity for 1,2-propanediol was 5.1 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 7

2.0 g of sponge-Ni catalyst (trade name: R-200, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of methanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted



three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and  
5 thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the  
10 same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was  
15 conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the  
20 contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the  
25 resultant GC chart, the conversion of glycidol was 81.4 %, the selectivity for 1,3-propanediol was 61.1 % and the selectivity for 1,2-propanediol was 2.9 %. Further, according to the GC analysis, peaks corresponding to 3-  
30 hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 8

2.0 g of sponge-Ni catalyst (trade name: R-200, mfd. by Nikko Rika K.K.) wetted with water was transferred to  
35 an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was

added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of ethanol and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 78.2 %, the selectivity for 1,3-propanediol was 61.1 % and the selectivity for 1,2-propanediol was 6.9 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 9

2.0 g of a sponge-Co catalyst (trade name: R-400, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd.

by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of dioxane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 79.9 %, the selectivity for 1,3-propanediol was 53.6 % and the selectivity for 1,2-propanediol was 8.4 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 10

2.0 g of a sponge-Co catalyst (trade name: R-400, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of dioxane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 400 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 91.2 %, the selectivity for 1,3-propanediol was 57.9 % and the selectivity for 1,2-propanediol was 9.1 %. Further, according to the GC analysis, peaks corresponding to 3-

hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 11

2.0 g of a sponge-Co catalyst (trade name: R-400, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of dioxane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 0.8 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 87.2

%, the selectivity for 1,3-propanediol was 54.5 % and the selectivity for 1,2-propanediol was 8.2 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 12: preparation of Co catalyst carried on silica carrier

5.480 g of cobalt nitrate hexahydrate was weighed in a beaker, and 9.00 g of deionized water was added to the beaker to thereby prepare Aqueous Solution (1). Then, 10.00 g of silica carrier (CARICT Q-15 mfd. by Fuji Silysia Chemical LTD) was added to the beaker containing Aqueous Solution (1) which had been prepared therein, so as to cause the entire amount of Aqueous Solution (1) to be absorbed into the silica carrier.

The resultant silica carrier which had absorbed therein Aqueous Solution (1) was dried at 100°C for one hour under a stream of nitrogen. The drying was carried out under a stream of nitrogen at a space velocity 2400 h<sup>-1</sup> under atmospheric pressure. Then, the silica carrier was reduced at 400°C for two hours under a stream of hydrogen to thereby prepare a catalyst carrying metal-Co on the silica carrier. The reduction was carried out under a stream of hydrogen at a space velocity 2400 h<sup>-1</sup> under atmospheric pressure.

Example 13

The catalyst carrying metal-Co on the silica carrier, which had been prepared in Example 12, was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted

three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and  
5 thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the  
10 same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was  
15 conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the  
20 contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the  
25 resultant GC chart, the conversion of glycidol was 42.2 %, the selectivity for 1,3-propanediol was 67.6 % and the selectivity for 1,2-propanediol was 8.5 %. Further, according to the GC analysis, peaks corresponding to 3-  
30 hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 14: preparation of Co-K catalyst carried on silica carrier

5.490 g of cobalt nitrate hexahydrate and 0.021 g of  
35 potassium nitrate were weighed in a beaker, and 8.02 g of deionized water was added to the beaker to thereby prepare Aqueous Solution (2). Then, 10.00 g of silica

carrier (CARIACT Q-15) was added to the beaker containing Aqueous Solution (2) which had been prepared therein, so as to cause the entire amount of Aqueous Solution (2) to be absorbed into the silica carrier.

5           The resultant silica carrier which had absorbed therein Aqueous Solution (2) was dried at 100°C for one hour under a stream of nitrogen. Then, the silica carrier was reduced at 400°C for two hours under a stream of hydrogen, to thereby prepare a catalyst carrying  
10 metal-Co on the silica carrier.

Example 15

          The catalyst carrying metal-Co on the silica carrier, which had been prepared in Example 14 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having  
15 an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further  
20 repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and  
25 thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

          The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the  
30 same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was  
35 conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.



When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 40.0 %, the selectivity for 1,3-propanediol was 68.2 % and the selectivity for 1,2-propanediol was 9.1 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 16: preparation of Co-Te catalyst carried on silica carrier

5.488 g of cobalt nitrate hexahydrate and 0.027 g of telluric acid were weighed in a beaker, and 8.02 g of deionized water was added to the beaker to thereby prepare Aqueous Solution (3). Then, 10.01 g of silica carrier (CARIACT Q-15) was added to the beaker containing Aqueous Solution (3) which had been prepared therein, so as to cause the entire amount of Aqueous Solution (3) to be absorbed into the silica carrier.

The resultant silica carrier which had absorbed therein Aqueous Solution (3) was dried at 100°C for one hour under a stream of nitrogen. Then, the silica carrier was reduced at 400°C for two hours under a stream of hydrogen, to thereby prepare a catalyst carrying metal-Co on the silica carrier.

Example 17

The catalyst carrying metal-Co on the silica carrier, which had been prepared in Example 16 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking.

Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

10       The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

20       When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

25       As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 52.9 %, the selectivity for 1,3-propanediol was 51.9 % and the selectivity for 1,2-propanediol was 7.6 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

35       Example 18

      The catalyst carrying metal-Co on the silica carrier, which had been prepared in Example 12, was

transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking.

5 Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement.

10 The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the

15 contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the

20 autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 100°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

25 When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the

30 supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 75.7 %, the selectivity for 1,3-propanediol was 50.9 % and the

35 selectivity for 1,2-propanediol was 8.2 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propion-

aldehyde as carbonyl compounds were not detected.

Example 19

The catalyst carrying metal-Co on the silica carrier, which had been prepared in Example 12 was  
5 transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from  
10 the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained  
15 was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with  
20 nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 2.4 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature  
25 in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was  
30 cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

35 As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 35.3

%, the selectivity for 1,3-propanediol was 65.8 % and the selectivity for 1,2-propanediol was 9.4 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 20

The catalyst carrying metal-Co on the silica carrier, which had been prepared in Example 12 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 2.4 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 60°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the

supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 19.3 %, the selectivity for 1,3-propanediol was 78.4 % and the selectivity for 1,2-propanediol was 7.6 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

10 Example 21: preparation of Ru catalyst carried on silica carrier

6.630 g of an aqueous ruthenium nitrate solution containing 3.969 wt. % (mass %) of ruthenium was weighed in a beaker, and was used as Aqueous Solution (4). Then, 10.00 g of silica carrier (CARIACT Q-15) was added to the beaker containing therein Aqueous Solution (4), so as to cause the entire amount of Aqueous Solution (4) to be absorbed into the silica carrier.

The resultant silica carrier which had absorbed therein Aqueous Solution (4) was dried at 100°C for one hour under a stream of nitrogen. Then, the silica carrier was reduced at 400°C for two hours under a stream of hydrogen, to thereby prepare a catalyst carrying metal-Ru on the silica carrier.

25 Example 22

The catalyst carrying Ru on the silica carrier, which had been prepared in Example 21 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained

was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

5 The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the  
10 autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

15 When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the  
20 supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 16.1 %, the selectivity for 1,3-propanediol was 57.3 % and the  
25 selectivity for 1,2-propanediol was 19.7 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 23

30 2.0 g of a sponge-Co catalyst (trade name: R-400, mfd. by Nikko Rika K.K.) wetted with water was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was  
35 added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further

repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained  
5 was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with  
10 nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature  
15 in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was  
20 cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 83.3 %, the selectivity for 1,3-propanediol was 64.3 % and the selectivity for 1,2-propanediol was 12.0 %. Further,  
30 according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 24

2.0 g of a sponge-Co catalyst (trade name: R-400, mfd. by Nikko Rika K.K.) wetted with water was  
35 transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having



an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 2.4 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 60°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 83.1 %, the selectivity for 1,3-propanediol was 65.1 % and the selectivity for 1,2-propanediol was 12.5 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 25: preparation of Ni catalyst carried on silica

carrier

2.752 g of nickel nitrate hexahydrate was weighed in a beaker, and 3.50 g of deionized water was added to the beaker to thereby prepare Aqueous Solution (5). Then, 5.00 g of silica carrier (CARIACT Q-15) was added to the beaker containing Aqueous Solution (5) which had been prepared therein, so as to cause the entire amount of Aqueous Solution (5) to be absorbed into the silica carrier.

The resultant silica carrier which had absorbed therein Aqueous Solution (5) was dried at 100°C for one hour under a stream of nitrogen. Then, the silica carrier was reduced at 400°C for two hours under a stream of hydrogen, to thereby prepare a catalyst carrying metal-nickel carried on the silica carrier.

Example 26

The catalyst carrying Ni carried on the silica carrier, which had been prepared in Example 25 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the

autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 100°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 74.9 %, the selectivity for 1,3-propanediol was 41.9 % and the selectivity for 1,2-propanediol was 53.3 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 27

The catalyst carrying Ni carried on the silica carrier, which had been prepared in Example 25 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with

nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 120°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 96.9 %, the selectivity for 1,3-propanediol was 57.5 % and the selectivity for 1,2-propanediol was 35.4 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 28

The catalyst carrying Ni carried on the silica carrier, which had been prepared in Example 25 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of

dioxane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 120°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 98.8 %, the selectivity for 1,3-propanediol was 61.5 % and the selectivity for 1,2-propanediol was 29.6 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 29

The catalyst carrying Ni carried on the silica carrier, which had been prepared in Example 25 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of

ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of dioxane and 5.00 g of glycidol were added thereto.

5       The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 2.4 MPa (gauge pressure) was finally applied to the  
10       autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 120°C for 5 hours. During the reaction,  
15       hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

      When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the  
20       supernatant was removed from the autoclave and the supernatant was analyzed by GC.

      As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 99.0  
25       %, the selectivity for 1,3-propanediol was 57.5 % and the selectivity for 1,2-propanediol was 35.5 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

30       Example 30

      The catalyst carrying Ni carried on the silica carrier, which had been prepared in Example 25 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having  
35       an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from

the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of dioxane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of dioxane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 140°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 100 %, the selectivity for 1,3-propanediol was 64.2 % and the selectivity for 1,2-propanediol was 20.0 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

Example 31: preparation of Urushibara-Co catalyst (U-Co-BA)

10 g of aluminum powder (40-80 mesh) was added into a 500 ml-beaker, and 50 ml of 1 %-aqueous sodium hydroxide solution was added thereto, and the resultant

mixture was stirred at room temperature (about 25°C) for 10 minutes. Thereafter, the resultant supernatant was removed from the beaker, and further the residue was washed twice with 30 ml of hot water.

5           5 ml of water was added to the residue, and the resultant mixture was heated to 95°C, and thereafter was cooled to 40°C. Then, an aqueous solution of cobalt chloride hexahydrate (which had been obtained by dissolving 8.1 g of cobalt chloride hexahydrate in 18 ml  
10 of water) was added to the beaker, and the resultant mixture was subjected to a reaction by elevating the temperature thereof to 55°C. After the completion of the reaction, the reaction product was washed twice with 100 ml of hot water. 30 ml of water was added to the  
15 residue, and while the resultant mixture was cooled with ice, 250 ml of 20%-aqueous sodium hydroxide solution was added slowly to the mixture so that the temperature did not exceed 60°C. After the completion of the addition, the resultant mixture was heated to 50°C, and the  
20 stirring thereof was continued. When the production of hydrogen was terminated, the stirring was stopped, and the resultant supernatant was removed from the reaction mixture. Then, the residue was washed five times with 100 ml of hot water (until the supernatant showed  
25 neutrality), to thereby obtain a Co catalyst which had been suspended in water (amount: 2 g as metal Co).

#### Example 32

          The Urushibara-Co catalyst (U-Co-BA) , which had been prepared in Example 31 was transferred to an  
30 autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter, the resultant supernatant was removed from the autoclave  
35 by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in



place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen, sequentially, in the same manner as in Example 1, and a hydrogen pressure of 1.6 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 76.9 %, the selectivity for 1,3-propanediol was 69.0 % and the selectivity for 1,2-propanediol was 8.5 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Example 33

The Urushibara-Co catalyst (U-Co-BA) , which had been prepared in Example 31 was transferred to an autoclave made of stainless steel (mfd. by Taiatsu Glass K.K.) equipped with a stirrer and having an internal volume of 120 ml, then 20 ml of ethanol was added to the catalyst and thoroughly mixed under shaking. Thereafter,

the resultant supernatant was removed from the autoclave by decantation. This operation was further repeated twice, and then the same operation was conducted three times except for using 20 ml of 1,2-dimethoxyethane in place of ethanol to effect the solvent replacement. The resultant supernatant which had finally been obtained was removed from the catalyst by decantation, and thereafter, 30 g of 1,2-dimethoxyethane and 5.00 g of glycidol were added thereto.

The reactor was tightly closed, and then the contents (atmosphere) of the autoclave were replaced with nitrogen, and further with hydrogen sequentially in the same manner as in Example 1, and a hydrogen pressure of 2.4 MPa (gauge pressure) was finally applied to the autoclave. Subsequently, while the contents of the autoclave were being stirred at 800 rpm, the temperature in the autoclave was elevated and the reaction was conducted at 80°C for 5 hours. During the reaction, hydrogen was introduced into the autoclave so as to maintain the reaction pressure at a constant level.

When the reaction was completed, the reactor was cooled to room temperature and depressurized, and the contents of the autoclave were replaced with nitrogen, and then the reactor was opened. Thereafter, the supernatant was removed from the autoclave and the supernatant was analyzed by GC.

As a result of the calculation from the peak area ratios between the respective peaks appearing in the resultant GC chart, the conversion of glycidol was 99.8 %, the selectivity for 1,3-propanediol was 67.6 % and the selectivity for 1,2-propanediol was 7.8 %. Further, according to the GC analysis, peaks corresponding to 3-hydroxypropionaldehyde, hydroxyacetone and propionaldehyde as carbonyl compounds were not detected.

#### Industrial Applicability

As described hereinabove, a both end-hydroxyl group-

terminated diol (e.g., propanediol) having an extremely low carbonyl impurity content can be produced with high efficiency, by using the catalyst for producing the both end-hydroxyl group-terminated diols, or the process for  
5 producing the both end-hydroxyl group-terminated diols by using the catalyst according to the present invention.

Further, the both end-hydroxyl group-terminated diols which can be obtained by the production process for such diols (particularly, 1,3-propanediol) according to  
10 the present invention have a high purity as compared with the 1,3-propanediols which had been obtained by conventional methods. When the thus obtained both end-hydroxyl group-terminated diols are used as a starting material for resins such as polyester, it is clear that a  
15 resin having little odor or coloring can be inexpensively produced.

CLAIMS

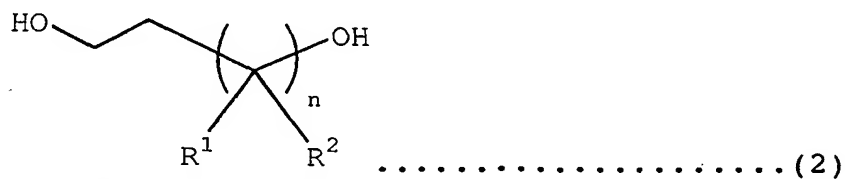
1. A catalyst which contains at least one element selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table, and is to be used for  
 5 subjecting an epoxy alcohol represented by the following general formula (1) to a hydrogenolysis reaction in the presence of at least one solvent selected from the group  
 10 consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the  
 following general formula (2).

15 General formula (1):



(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl  
 20 group having 6 to 13 carbon atoms and n represents an integer of 1 to 6);

General formula (2):



(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, a cycloalkyl group, an aryl group or an alkyl  
 25 group having 1 to 8 carbon atoms, and n represents an integer of 1 to 6).

2. A catalyst for producing both end-hydroxyl group-terminated diols according to claim 1, which  
 30 comprises at least one element selected from the group

consisting of Fe, Co, Ni, Cu, Re and Ru.

3. A catalyst for producing both end-hydroxyl group-terminated diols according to claim 1 or 2, which is a sponge-type catalyst.

5 4. A catalyst for producing both end-hydroxyl group-terminated diols according to claim 1 or 2, which is a carrier-type catalyst.

10 5. A catalyst for producing both end-hydroxyl group-terminated diols according to claim 4, wherein the carrier comprises as least one species selected from the group consisting of: activated carbon, alumina, silica, silica alumina, zeolite, diatomaceous earth, titania, and zirconia.

15 6. A process for producing a catalyst for producing both end-hydroxyl group-terminated diols according to claim 3, which comprises at least the following Step (A) and Step (B):

20 Step (A): a step of producing an alloy of aluminum and at least one element selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table;

25 Step (B): a step of eluting aluminum from the alloy obtained in Step (A), to thereby produce a catalyst for producing both end-hydroxyl group-terminated diols.

30 7. A process for producing a catalyst for producing both end-hydroxyl group-terminated diols according to claim 4 or 5, which comprises at least the following Step (C) and Step (D):

35 Step (C): a step of causing at least one element or a compound containing the at least one element to be carried on a carrier, the element being selected from the group consisting of Group V elements, Group VI elements, Group VII elements, Group VIII elements, Group IX elements, Group X elements, and Group XI elements in the periodic table, to thereby produce a carrier carrying

thereon the at least one element;

Step (D): a step of hydrogenating the at least one element carried on the carrier obtained in Step (C), to thereby produce a catalyst for producing both end-hydroxyl group-terminated diols.

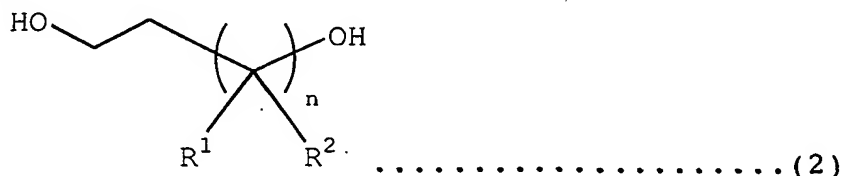
8. A process for producing a both end-hydroxyl group-terminated diol, wherein an epoxy alcohol represented by the following general formula (1) is subjected to a hydrogenolysis reaction in the presence of a catalyst for producing both end-hydroxyl group-terminated diols according to any of claims 1-5, in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the following general formula (2).

General formula (1):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6);

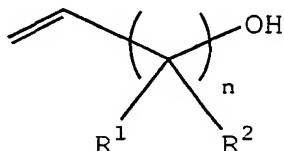
General formula (2):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, a cycloalkyl group, an aryl group or an alkyl group having 1 to 8 carbon atoms, and  $n$  represents an integer of 1 to 6).

9. A process for producing a both end-hydroxyl group-terminated diol according to claim 8, wherein the epoxy alcohol represented by the following general formula (1) is a compound which has been obtained by the epoxidizing an unsaturated alcohol compound represented by formula (3):

General Formula (3):



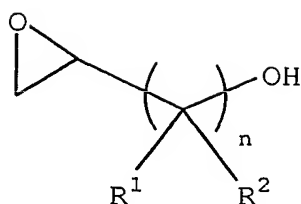
(wherein R<sup>1</sup> and R<sup>2</sup> each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and n represents an integer of 1 to 6).

10. A process for producing a both end-hydroxyl group-terminated diol represented by the general formula (2), which comprises at least the following Step (E) and Step (F):

Step (E): a step of epoxidizing an unsaturated alcohol compound represented by general formula (3), to thereby obtain an epoxy alcohol represented by the general formula (1);

Step (F): a step of subjecting the epoxy alcohol compound to a hydrogenolysis reaction in the presence of a catalyst for producing a both end-hydroxyl group-terminated diols according to any of claims 1-5, and in the presence of at least one solvent selected from the group consisting of ethers, esters, aromatic hydrocarbon compounds, alicyclic hydrocarbon compounds and aliphatic hydrocarbon compounds, to thereby obtain a both end-hydroxyl group-terminated diol represented by the following general formula (2).

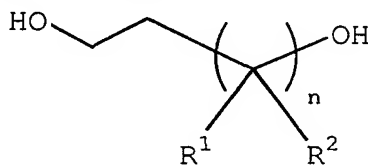
General formula (1):



..... (1)

(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6);

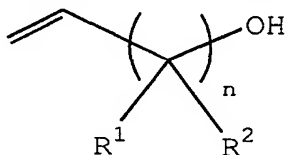
General formula (2):



..... (2)

(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6)

General Formula (3):



(wherein  $R^1$  and  $R^2$  each independently represents hydrogen, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 3 to 10 carbon atoms, or an aryl group having 6 to 13 carbon atoms and  $n$  represents an integer of 1 to 6);

11. A process for producing a both end-hydroxyl group-terminated diol according to any of claims 8-10, wherein the epoxy alcohol represented by the following general formula (1) is at least one epoxy alcohol compound selected from the group consisting of: glycidol, 3,4-epoxy-1-butanol and 3,4-epoxy-2-butanol.

12. A process for producing a both end-hydroxyl



group-terminated diol according to claims 9 or 10,  
wherein the an unsaturated alcohol compound represented  
by general formula (3) is at least one unsaturated  
alcohol compound selected from the group consisting of:  
5 allyl alcohol, 3-buten-1-ol and 3-buten-2-ol.

13. A process for producing a both end-hydroxyl  
group-terminated diol according to any of claims 8-12,  
wherein the solvent is at least one species selected from  
the group consisting of diethyl ether, dibutyl ether,  
10 ethylene glycol dimethyl ether, ethylene glycol diethyl  
ether, 1,4-dioxane, benzene, toluene, xylene,  
cyclohexane, hexane, ethyl acetate, propyl acetate,  
isopropyl acetate and butyl acetate.

14. A both end-hydroxyl group-terminated diol,  
15 which has been produced by a process for producing a both  
end-hydroxyl group-terminated diol according to any of  
claims 8-13.

## INTERNATIONAL SEARCH REPORT

 Int. Application No  
 PCT/JP 02/02797

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 B01J23/00 C07C29/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 975 449 A (SUZUKI SHIGETO) 17 August 1976 (1976-08-17) column 1, line 41 -column 4, line 10; example 6	1-14
X	US 2 895 819 A (STUART FIEDLER WILLIAM) 21 July 1959 (1959-07-21) column 1, line 15 - line 41	1-3,6
X	GB 970 790 A (HENKEL & CIE GMBH) 23 September 1964 (1964-09-23) column 2, line 69 -column 3, line 10; table 3	1-5,7
A	US 4 590 313 A (GREY ROGER A ET AL) 20 May 1986 (1986-05-20) the whole document	1-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

18 June 2002

Date of mailing of the international search report

22/07/2002

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# INTERNATIONAL SEARCH REPORT

Int. Application No.  
PCT/JP 02/02797

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

Int'l Application No

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